

Quantum and semi-classical depopulation cross sections : collisions of low-Rydberg alkali atoms with ground state He atoms

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Received 2 June 1999, accepted 10 June 1999

Abstract A two-channel model calculation of quantum-mechanical and semi-classical depopulation cross sections for the collision of Li(7s) by the ground state He atom in the sub-eV energy region has been reported. Comparison with a similar prior study of Saha and Lane [1994] reveals an improved agreement between semi-classical and quantal cross sections for Li(7s) + He over Na(8s) + He. This close agreement suggests that the relative motion whether described classically or quantum-mechanically is not very important except at very low energies. For the Li(7s) + He collisions, the strong coupling enhances the depopulation cross sections. Both the magnitudes and the energy dependence of the cross sections depend on the details of the collision dynamics ; any generalization in terms of the asymptotic energy separations of the adiabatic potentials is inappropriate. The strength of the couplings controls the dynamics, and is found to determine the sharpness of the observed intracollisional interference structures in the cross sections.

Keywords : Depopulation cross section, Li(7s) + He collision, two-channel model calculation

PACS No. : 34.60.+z

The domain of collision processes involving Rydberg atoms is limitless in variety and complexity. Rydberg atoms are highly excited atoms. Their energy spectrum can be determined by Rydberg series characterized by an effective quantum number $n_{eff} = n - \delta$, where δ is the well-known quantum defect [1]. At very high levels of excitation, the high-Rydberg regime, the electron interacts weakly with the inner shells. For collisions involving high-Rydberg atom, the excited electron can be described as colliding with the collision partner, the *perturber*, independent of the presence of the ion *core* (Binary encounter approximation [2]), the electron collision can be assumed to occur in a time short compared to the period of the bound Rydberg electron

(Impulse approximation [3]) and the electron can be treated as *free* from the Coulombic influence of the core during its encounter with the perturber (*Free Electron approximation* [4]). All of these approximations led to the powerful Fermi-theory [5]. The high-Rydberg collisions show general trends that depend primarily on the nature of the colliding partner, in particular, how it interacts with a slow electron. Although there have been many refinements of Fermi's theory and many theoretical studies of high-Rydberg collisions [5], only a few serious theoretical efforts [6-8] have been made up to now to tackle the low-Rydberg ($n \leq 10$) atom collision problems.

Low-Rydberg collisions are very sensitive to the details of the interactions. It demands a much sophisticated approach where the full three-body interactions involving the *perturber*, the distant *electron*, and the compact *core* are treated accurately. The semi-classical Molecular Orbital (MO) approximation [6] provides a very convenient, yet rigorous, way to estimate the total depopulation cross sections of the low-Rydberg atoms colliding with neutral perturbers in the sub-eV energy regime. Such approximations have been successfully employed to evaluate not only the total quenching of the parent Rydberg Na and Rb atoms, but also the state-selective transitions responsible for the process [7-12]. Since these investigations are extended to very low energies, the question still remains – *is a semi-classical description appropriate to thermal energies* ? Saha and Lane [8] have made the first attempt to shed light into this aspect through a model two-state quantal calculation ; they have calculated the depopulation cross sections for the Na(8s) + He collisions. Considering the most probable transition, namely Na(8s) \rightarrow Na (7p), they have demonstrated that a semi-classical MO approach is as reliable as a full quantal approximation, except at very low energies ($v \leq 0.004$ a.u.) where quantal effects are bound to manifest. *Whether their findings can be generalised to other pseudo-one-electron targets, or how much does the target core influence the outcome of the state-changing interactions are yet not known.* We, in this letter, intend to answer these questions through a study of Li(7s) + He collisions using a similar quantum-mechanical treatment [8] that explicitly includes the quasi-molecule formation. In terms of quantum defects, Li(7s) ($n_{eff} = 6.6$) is only a bit more deviated from the true hydrogenic state as compared to Na(8s) ($n_{eff} = 6.652$). At thermal velocities, the process of excitation, similar to the Na(8s) + He scattering, is expected to make very little contribution towards quenching the Li(7s) state. The process of de-excitation, in this pair, will, however, populate the neighbouring 6f states of Li ; the asymptotic energy defect for this transition is $\Delta E(R \rightarrow \infty) = 2.41 \times 10^{-3}$ a.u. . This is slightly larger than the asymptotic energy defect for the transition Na(8s) \rightarrow Na (7p) [$\Delta E(R \rightarrow \infty) = 1.93 \times 10^{-3}$ a.u.]. A comparative study of these two pairs *via* the full quantum-mechanical and semi-classical calculation will enable us not only a way to see how the minute details of the collision dynamics affect the outcome of these state-changing collisions, but also to assess the reliability of the semi-classical approximation for such investigations. In the present letter, we investigate the following transition :



using our model two-state calculations. Due to this two-state approximation the present results may not represent the true collision dynamics as the influence of the other neighbouring states are not included. However, our intention here is to analyse *the role of the relative nuclear motion* ; we anticipate that this relative motion whether described classically or quantum mechanically will not be very important at low energies, *e.g.*, in the threshold region where the amount of the kinetic energy transferred between the electron and the nuclei is not negligible when compared with the collision energy.

In a Molecular Orbital (MO) approach the colliding pair is represented through a transient quasi-molecule $[(\text{LiHe})^+ - e^-]$, whose adiabatic potential energy surfaces will represent the entrance, as well as all possible important final channels of the reaction. The technique of the pseudo potential [13] is invoked to simulate the effective binding of the Rydberg electron in this quasi-molecule. A Linear Combination of Atomic Orbitals (LCAO) is used to obtain the electronic wave function. In the quantum-mechanical approximation, both the nuclear motion and the electron motion are treated quantum mechanically, and the system is described by the time-independent Schrödinger equation [6] :

$$H(\mathbf{R}, \mathbf{r}) \psi(\mathbf{R}, \mathbf{r}) = E \psi(\mathbf{R}, \mathbf{r}) \quad (2)$$

To obtain the solution of the above equation we expand the system wave function in terms of the nuclear wave functions $\chi_n(\mathbf{R})$, the electronic wave functions $\phi_n(\mathbf{R}, \mathbf{r})$, and the Electron translation factor (ETF) $F_n(\mathbf{R}, \mathbf{r})$ (see Ref. [6] for details). Substituting this into eq. (2), we obtain, after some simplifications, a set of coupled equations (in the notations of Ref. [6])

$$\left\{ (1/2\mu) [-i\hbar \Delta + (\mathbf{P} + \mathbf{A})]^2 + h - EI \right\} \chi_n(\mathbf{R}) = 0 \quad (3)$$

The set of above equations can be transformed into a more convenient form by using the diabatic basis [14]. For numerical calculation, this form effects a considerable simplifications in the numerical procedure since the first order derivatives are absent. This is equivalent to the diabatic representation of Smith [15] (see also Refs. 16 and 17). In this model calculation the coupling between the initial Li(7s Σ) and the final Li(6fE) molecular symmetries is retained. The nuclear wave functions $\chi_n(\mathbf{R})$ can be written as

$$\phi(\mathbf{R}) = \mathbf{C}(\mathbf{R}) \chi_n(\mathbf{R}), \quad (4)$$

where the transformation matrix $\mathbf{C}(\mathbf{R})$ is determined numerically by solving the following differential equations

$$d\mathbf{C} / dR + \mathbf{D}\mathbf{C} = 0, \quad (5a)$$

where \mathbf{C} satisfies the boundary condition

$$\mathbf{C}(\infty) = \mathbf{I}. \quad (5b)$$

Here \mathbf{I} refers to the identity matrix ; the matrix elements $D_{ij} (= \mathbf{P} + \mathbf{A})$ are given by

$$D_{ij} = \begin{cases} \langle j | d/dR | i \rangle & \text{for } i \neq j \\ 0 & \text{for } i = j \end{cases} \quad (5c)$$

In the diabatic representation [according to Delos [18], it is the P -diabatic representation], the radial partial wavefunctions satisfy for each J , the following coupled differential equations :

$$\left[\left\{ d^2 / dR^2 - J(J+1) / R^2 \right\} \mathbf{I} - 2\mu V^d + 2\mu E \right] \phi(R) = 0. \quad (6)$$

Here the diabatic potential $V^d(R)$ is given by

$$V^d(R) = \mathbf{C}^{-1}(R) \epsilon(R) \mathbf{C}(R) \quad (7)$$

where $\varepsilon(R)$ is the diagonal eigen-value matrix of the molecular Hamiltonian \hat{h} . For a 2-channel case, eq. (5a) can be solved analytically [14], and is given by

$$C(R) = \begin{pmatrix} \cos \zeta(R) & \sin \zeta(R) \\ -\sin \zeta(R) & \cos \zeta(R) \end{pmatrix}, \quad (8)$$

where

$$\zeta(R) = \int D_{ij} dR, \quad j \neq i. \quad (9)$$

By making the usual partial wave decomposition, the radial part of the coupled eq. (6) can be solved numerically. Making use of the log derivative method of Johnson [19], we obtain the S-matrix; the cross sections are then calculated by using the following well known relation [20]:

$$\sigma_{ij} = \left(\pi / k_i^2 \right) \sum J(J+1) |S_{ij}^J|^2 \quad (10)$$

where $k_i^2 = 2\mu E$ and E is the collision energy.

To construct the molecular orbitals a sufficiently large basis set containing all excited states up to 10s of Li are included in the calculation; we retain 20 and 17 configuration interaction (CI), respectively, to generate these molecular Σ and Π states. The adiabatic potential surfaces correlated to the initial and final channels, Li(7s) Σ and Li(6f) Σ are shown in Figure 1; the corresponding states for the Na(8s) + He scattering [8] are also kept for comparison. The Li(7s)-He pair (Figure 1) exhibits a very strong avoided crossing in the vicinity of $R \approx 10 a_0$; ΔE

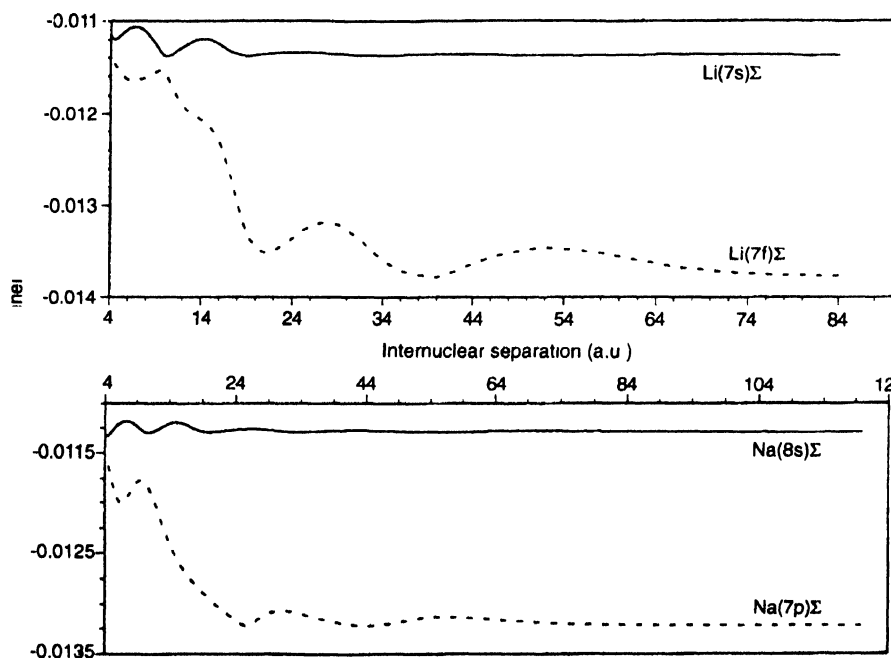


Figure 1. Adiabatic potential energy curves for Li(7s) + He and Na(8s) + He collisions [4]. Different Σ states are shown separately.

for this endoergic transition is only 1.8×10^{-4} a.u.. The Na + He system also produces a near crossing around the same R region; the amount of energy defect in this case is, however, more than double [$\Delta E(R \approx 10 a_0) = 4.92 \times 10^{-4}$ a.u.]. The Li(7s) Σ and Li(6f) Σ states also couple together at larger R (≈ 30 and $55 a_0$), but with significantly reduced strength. In the Na + He scattering (see Fig. 1) there is, however, no such long-range coupling.

In Figure 2, the diabatic potentials for only reaction (1) are depicted along with their adiabatic counterparts. The adiabatic matrix elements (not shown) involving the initial Li(7s) Σ and final Li(6f) Σ states exhibit rapid variation in the region of avoided crossings; it is small elsewhere. The transformation parameter $\zeta(R)$, defined in Eq. (9), renders very small contribution until the avoided crossing region is reached; it increases to a finite value after which it starts decreasing again. Such behaviour is expected since at each avoided crossing, the mixing of the two states interchanges their characters [14]. In contrast to the adiabatic curves, the diabatic curves cross in the region of strong adiabatic coupling. As seen in Figure 2, after the crossing they tend to merge again with the adiabatic curves. The resulting diabatic coupling matrix elements (not shown) varies slowly with R in the strong interaction region. They couple very weakly and as a result, this representation provides a much more accurate description [14] of the slow collision process.

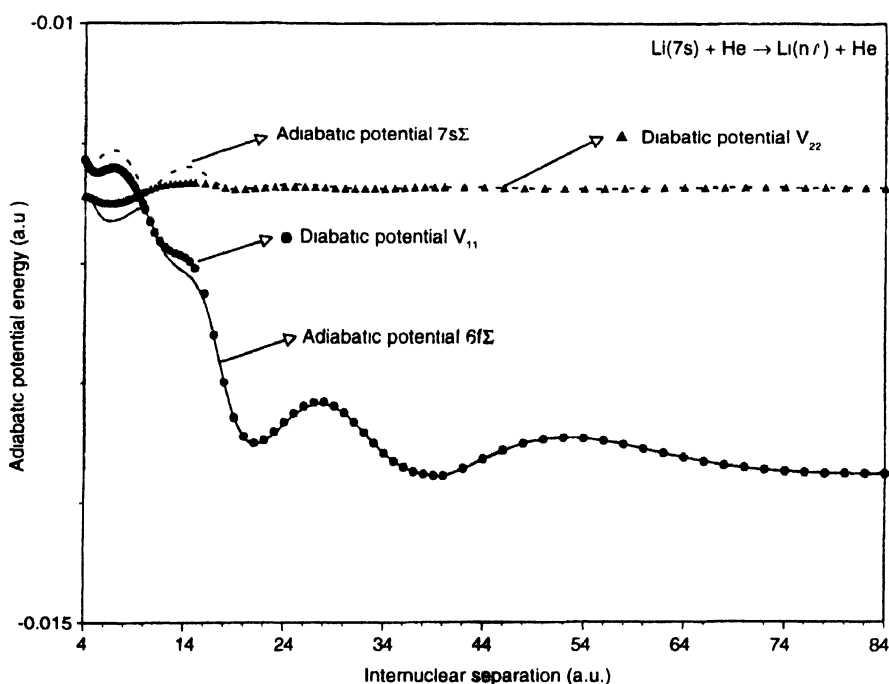


Figure 2. Adiabatic and diabatic potential energy curves for Li(7s) + He collisions.

Figure 3 depicts the depopulation cross section of the parent Li(7s) and Na(8s) states [8]. The corresponding 2-channel semi-classical results for both systems are compared in the same figure. The total cross section for the depopulation of the Li(7s) state, after exhibiting a flat regions around $\nu \approx 8 \times 10^{-4}$ a. u., decreases sharply to attain a minimum value at $\nu \approx 3 \times 10^{-3}$ a. u.. Then another mild peak in the cross section is observed around $\nu \approx 9 \times 10^{-3}$ a. u.. The quantal cross sections show very good agreement with the two-state semi-classical results. This clearly demonstrates the ability of the semi-classical approach to yield reliable estimates

of the depopulation cross sections. New possibilities of investigating the total annihilation of the low-Rydberg Li atoms colliding with the ground state He at sub-eV energy regime where transitions to all neighbouring channels are probable can be explored easily. Since a fully converged multi-channel quantal calculation is expected to be prohibitively expensive in terms of computer time, the above outcome regarding the reliability of the semiclassical approach will enable us to tackle these important, yet thoroughly unstudied, problems, in the low-Rydberg domain easily.

The earlier results of Saha and Lane [8] for the depopulation of the Na(8s) state colliding with the same perturber, the He atoms, in the identical velocity regime are also shown in Figure 3. A comparison between the two apparently similar colliding partners clearly shows that the process of de-excitation of the low-Rydberg alkali metal atoms is governed primarily by the details of the collision dynamics, and any attempt for its generalization in terms of the asymptotic energy defects may be misleading. For example, we see that instead of the asymptotic energy defect, it is the energy difference at finite R values, along with the actual shape of the potential energy surfaces that determine not only the magnitudes of the total depopulation cross sections but also their velocity dependence. As noted earlier, the asymptotic energy defect for the de-excitation in the Na + He collision is comparatively smaller than its Li + He counterpart. Still the peak value of the cross section in the investigated velocity region is found to be larger for the Li + He scattering. This suggests that the stronger coupling that we observe for this pair around $R \approx 10 a_0$ leads to a larger probability of quenching of the parent state.

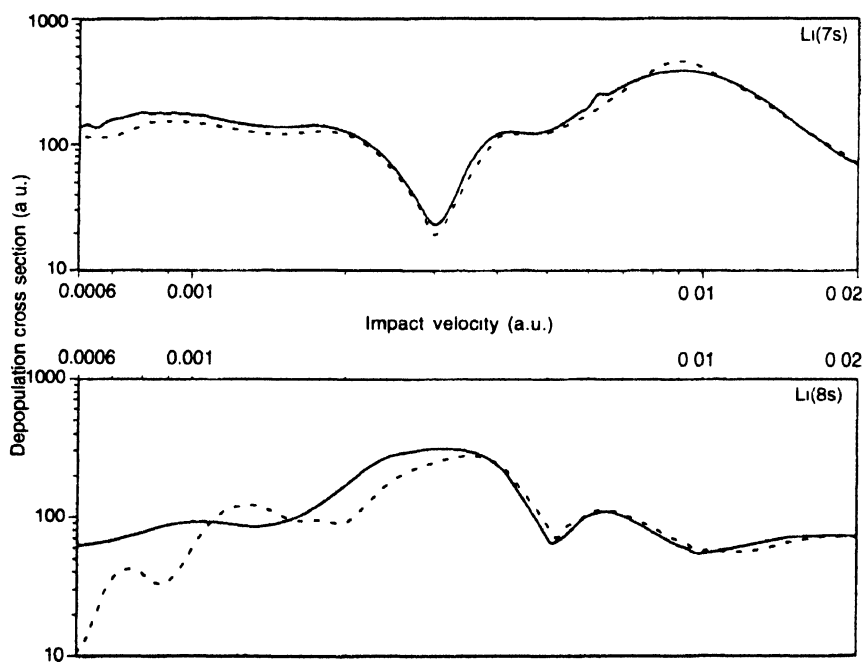


Figure 3. Cross sections for depopulation of Li(7s) and Na(8s) colliding with the ground state He atoms. *Full line* : Quantum-mechanical calculation ; *Dotted line* : Semi-classical calculation. Na(8s) results are from Ref. [8].

In their study, Saha and Lane [8] have noted that the avoided crossing around $R \approx 10 a_0$ is primarily responsible for the observed Stueckelberg interference structures [21, 22] in the

depopulation cross sections. In the semi-classical approach, this oscillation appears to be more pronounced in the Na + He scattering in the lower domain of our investigated velocity regime. Saha and Lane have observed that these sharper features in the cross section are a direct outcome of a comparatively weaker interaction between the two $[\text{Na}(8s)\Sigma$ and $\text{Na}(7p)\Sigma]$ coupled channels. For the Li (7s) + He collision the present findings also support their predictions; the stronger coupling around $R \approx 10 a_0$, along with the presence of long-range couplings between the two channels ($\text{Li}(7s)\Sigma$ and $\text{Li}(6f)\Sigma$) results into smoother interference features. This also agrees well with the less sharp Stueckelberg oscillations reported earlier [8].

Another point is worth noting here ; a comparatively better agreement between the quantal and semi-classical results for the Li+He scattering ; throughout the investigated velocity regime both cross sections are nearly identical. The strength of the coupling between the two molecular states is primarily responsible for this feature. Comparatively weaker coupling in the Na + He collision yields sharper interference effects, and the semi-classical results deviate appreciably as the pronounced quantal effects are not properly accounted for. Stronger coupling, however, in the Li + He scattering leads to a closer agreement between the cross sections obtained by the two approaches. The differences between the Li^+ and Na^+ core may also be responsible for determining the strength of the couplings. In order to observe the quantal effects in the Li + He collisions one must need to explore the very low velocity regime.

To conclude, we have reported a two-channel model calculation of quantum-mechanical and semi-classical depopulation cross sections for $\text{Li}(7s) + \text{He}$ collisions in the sub-eV energy regime. Our model calculation shows explicitly that the relative nuclear motion, whether described classically or quantum mechanically, is not that important except at very low energies, *e.g.*, in the region where the amount of kinetic energy transferred between the electron and the nuclei is not negligible compared with the collision energy. A comparative study with the earlier findings of the $\text{Na}(8s) + \text{He}$ scattering is also reported. The strength of the couplings is different in both the systems and consequently we found improved agreement between the semi-classical and quantal cross sections for $\text{Li}(7s) + \text{He}$ collisions over the $\text{Na}(8s) + \text{He}$ scattering. The magnitudes of the cross sections, as well as their velocity dependence, along with the manifestation of the intracollisional interference structures are found to be governed by the details of the collision dynamics ; any generalisation in terms of the asymptotic energy defects seems inappropriate. This excellent agreement between the quantal and the semi-classical results opens up the possibility of pursuing a detailed investigation on the low-Rydberg problems where both the endoergic and exoergic transitions are equally important. A detailed investigation along this is currently in progress and its findings will be reported shortly.

Acknowledgment

This research has been supported in part by the Research Corporation (B.C. S.), NSF CREST Cooperative agreement HDR-9707076, and the Army High Performance Computing Research Center under the auspices of the Department of Army, Army Research Laboratory Cooperative Agreement No. DAAHO4-95-C-008, the contract of which does not necessarily reflect the position of the Government, and no official endorsement should be inferred.

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